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ORIGINAL ARTICLE

Living polymerization of phenylacetylenes catalyzed by cationic rhodium complexes bearing tetrafluorobenzobarrelene

Masashi Shiotsuki[1], Naoya Onishi[1], Fumio Sanda[1] and Toshio Masuda[2]

Binary catalysts composed of cationic rhodium complexes, [(tfb)Rh(L)$_2$]X (tfb: tetrafluorobenzobarrelene, L: phosphine ligand, X: counter anion), and ^{i}PrNH$_2$ induced living polymerization of phenylacetylene and its ring-substituted derivatives. For instance, [(tfb)Rh(PPh$_3$)$_2$]BPh$_4$ in conjunction with ^{i}PrNH$_2$ polymerized phenylacetylene in a living manner to yield poly(phenylacetylene) with narrow molecular weight distribution (M_w/M_n 1.09) quantitatively. The living nature was confirmed by kinetic plots of the polymerization. Nuclear magnetic resonance studies revealed that ^{i}PrNH$_2$ serves to dissociate the coordinating PPh$_3$ ligand of [(tfb)Rh(L)$_2$]X to form an initiating species. Block copolymers were synthesized by the sequential polymerization of different phenylacetylenes using the present catalyst.

INTRODUCTION

Substituted polyacetylenes exhibit interesting properties and functions, including photoconductivity, electroluminescence, stimuli responsiveness, gas permeability and helical conformation,[1–5] which are mainly based on their conjugated and stiff main-chain structure. A great deal of effort has been made to develop new active catalysts that are effective for a wide range of acetylenic monomers and in precisely controlled polymerization. In the last decade, rhodium (Rh) catalysts have been commonly used for the synthesis of stereoregular polymers from monosubstituted acetylenes such as phenylacetylene (**1a**),[6,7] propiolic esters[8] and N-propargylamides.[9] Some of the Rh catalysts have been found to achieve living polymerization of monosubstituted acetylenes. The first example of Rh-catalyzed living polymerization of **1a** was reported by Kishimoto et al. using two catalyst systems, namely, [(nbd)Rh(C≡CPh)(PPh$_3$)$_2$]/DMAP (nbd: 2,5-norbornadiene, DMAP: 4-dimethylaminopyridine)[10,11] and [(nbd)Rh(μ-OMe)]$_2$/PPh$_3$/DMAP.[12] Another catalyst system for living polymerization, [(nbd)Rh(μ-OMe)]$_2$/1,4-bis(diphenylphosphino)butane, was proposed by Falcon et al.[13] Our group reported a ternary catalyst, [(nbd)RhCl]$_2$/PPh$_3$/LiC(Ph)=CPh$_2$.[14] A presumed active initiator, [(nbd)Rh{C(Ph)=CPh$_2$}{P(C$_6$H$_4$-p-F)$_3$}], can be isolated from the ternary system and can accomplish living polymerization of **1a** with virtually quantitative initiation efficiency (IE).[15] The living catalyst is also applicable to the living-like polymerization of N-propargylamides.[16]

Thus far we have exploited a new class of active Rh catalysts bearing a highly π-acidic diene ligand, tfb.[17–21] These tfb-bearing Rh catalysts feature higher activity in the polymerization of phenylacetylene-type monomers than do the conventional Rh catalysts bearing nbd. For instance, the polymerization of **1a** catalyzed by a zwitterionic tfb-Rh complex, (tfb)Rh$^+$[(η^6-Ph)B$^-$Ph$_3$] (**2**), proceeds much faster than that with the corresponding nbd analog, (nbd)Rh$^+$[(η^6-Ph)B$^-$Ph$_3$].[19]

In the course of further study on the tfb-Rh catalysts, we have recently found that a cationic Rh complex having two triphenylphosphine ligands, [(tfb)Rh(PPh$_3$)$_2$]BPh$_4$ (**3a**), in conjunction with amines polymerizes monomer **1a** in a living manner, as briefly reported in a communication.[21] The present article is a full paper dealing with detailed investigation of the living polymerization of **1a** and its ring-substituted derivatives with cationic tfb-Rh catalysts, including **3a** (Scheme 1).

## EXPERIMENTAL PROCEDURE
Instruments
Monomer conversions were determined by GC (Shimadzu, Kyoto, Japan, GC-14B, capillary column (CBP10-M25-025)); column temperature 125 °C, injection temperature 250 °C, internal standard tert-butylbenzene. The number- and weight-average molecular weights (M_n and M_w, respectively) and molecular weight distribution (MWD, M_w/M_n) of polymers were measured by gel permeation chromatography (GPC) with a JASCO PU-980/RI-930 chromatograph (JASCO, Tokyo, Japan); 40 °C, eluent tetrahydrofuran (THF),

[1]Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura Campus, Nishikyo-ku, Kyoto, Japan and [2]Department of Environmental and Biological Chemistry, Faculty of Engineering, Fukui University of Technology, Fukui, Japan
Correspondence: Professor M Shiotsuki, Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura Campus, Nishikyo-ku, Kyoto 615-8510, Japan.
E-mail: shiotsuki@adv.polym.kyoto-u.ac.jp
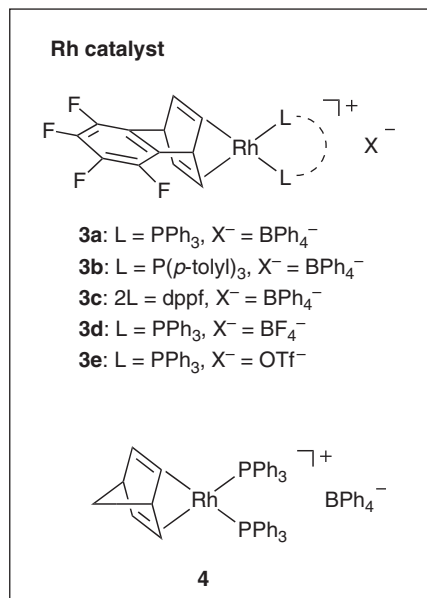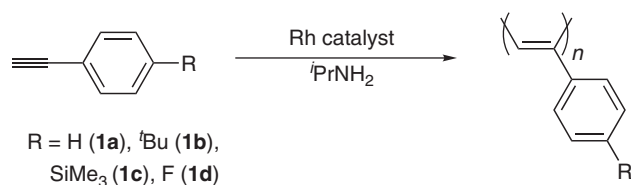
Scheme 1 Polymerization of **1a–d** with Rh catalysts/^{i}PrNH$_2$.

columns KF-805 (Shodex, Tokyo, Japan)×3, molecular weight limit up to 4×10^6, flow rate 1 ml min^{-1}; calibrated with polystyrene standards. ^{1}H (400 MHz), ^{13}C (100 MHz), ^{19}F (373 MHz) and ^{31}P (160 MHz) NMR spectra were all recorded on a JEOL ECX-400 spectrometer (JEOL, Tokyo, Japan) with chemical shifts referenced to internal standards CHDCl$_2$ (5.32 p.p.m., for ^{1}H NMR), CD$_2$Cl$_2$ (53.0 p.p.m., for ^{13}C NMR), and external standards P(OMe)$_3$ (140 p.p.m., for ^{31}P NMR), CFCl$_3$ (0 p.p.m., for ^{19}F NMR). High-resolution mass spectra (HRMS) were measured on a JEOL JMS-HX110A mass spectrometer (cationic complexes **3c–e** exhibited mass peaks consistent with their cationic moieties). Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials

Phenylacetylene (**1a**) was purchased (Aldrich, St Louis, MO, USA) and distilled over CaH$_2$ under reduced pressure before use. The metal complexes of (tfb)Rh$^+$[(η^6-Ph)B$^-$Ph$_3$] (**2**),[19] [(tfb)Rh(PPh$_3$)$_2$]BPh$_4$ (**3a**),[20] [(tfb)Rh{P (p-tolyl)$_3$}$_2$]BPh$_4$ (**3b**)[22] and [(nbd)Rh(PPh$_3$)$_2$]BPh$_4$ (**4**)[23] were synthesized according to the literature. NaBPh$_4$ (Aldrich), PPh$_3$ (Aldrich), AgBF$_4$ (Wako, Osaka, Japan), AgOTf (Wako), **1b** (Wako), **1c** (NOF, Tokyo, Japan) and **1d** (Wako) were purchased and used without further purification. Solvents were distilled by the standard procedures. ^{i}PrNH$_2$ and N,N,N',N'-tetramethylethylenediamine were purified by distillation over CaH$_2$.

[(tfb)Rh(dppf)]BPh$_4$ (3c)

A Schlenk tube equipped with a three-way stopcock was charged with (tfb)Rh$^+$[(η^6-Ph)B$^-$Ph$_3$] (50 mg, 0.077 mmol) and dppf (1,1'-bis(diphenylphosphino)ferrocene, 45 mg, 0.080 mmol) and filled with argon gas, to which CH$_2$Cl$_2$ (7.5 ml) was added. After the mixture was stirred at room temperature overnight, the solvent was removed under reduced pressure, and the formed orange powder was purified by recrystallization from CH$_2$Cl$_2$/Et$_2$O. The obtained solid was dried in *vacuo*. Yield: 71 mg (77%). ^{1}H NMR (CD$_2$Cl$_2$) δ: 7.72 (m, 8H), 7.59 (m, 12H), 7.32 (m, 8H), 7.01 (m, 8H), 6.86 (m, 4H), 5.65 (brs, 2H, bridgehead CH), 4.44 (br, 4H, Cp), 4.37 (brs, 4H, Cp) and 4.18 (m,

4H, sp^2-CH). ^{13}C NMR (CD$_2$Cl$_2$) δ: 164.1 (q, $^1J_{C-B}$=49.6 Hz, ipso C of BPh$_4$), 140.6 (dm, J=256 Hz, C-F of tfb), 139.0 (dm, J=248 Hz, C-F of tfb), 136.0 (Ph), 133.4 (Ph), 132.1 (Ph), 130.6 (Ph), 129.6 (Ph), 126.9 (m, ipso C of tfb), 125.6 (Ph), 121.7 (Ph), 83.2 (s, sp^2-C of tfb), 75.6 (m, α-C of Cp), 74.4 (s, β-C of Cp), 72.2 (m, ipso C of Cp) and 42.8 (s, bridgehead of tfb). ^{19}F NMR (CD$_2$Cl$_2$) δ: −145.8 (d, 2F, J=21.2 Hz C-F of tfb), −158.0 (d, 2F, J=21.6 Hz, C-F of tfb). ^{31}P NMR (CD$_2$Cl$_2$) δ: 27.7 (d, J_{Rh-P}=163 Hz). HRMS fast atom bombardment (FAB) calcd. for C$_{46}$H$_{34}$F$_4$FeP$_2$Rh (m/z): 883.0476, found: 883.0474.

[(tfb)Rh(PPh$_3$)$_2$]BF$_4$ (3d)

A Schlenk tube equipped with a three-way stopcock was charged with [(tfb)RhCl]$_2$ (30 mg, 0.041 mmol), PPh$_3$ (45 mg, 0.17 mmol) and AgBF$_4$ (18 mg, 0.092 mmol) and filled with argon gas, to which CH$_2$Cl$_2$ (4.0 ml) was added. After the mixture was stirred at room temperature for 5 h, the produced silver salt was removed by filtration. The solvent was removed from the filtrate under reduced pressure to afford orange powder. The formed solid was washed with Et$_2$O (2 ml×3 times) and then dried in *vacuo*. Yield: 73.5 mg (95%). ^{1}H NMR (CD$_2$Cl$_2$) δ: 7.58–7.31 (m, 30H), 5.87 (brs, 2H, bridgehead CH), 4.32 (m, 4H, sp^2-CH). ^{13}C NMR (CD$_2$Cl$_2$) δ: 140.5 (dm, J=241 Hz, C-F of tfb), 138.9 (dm, J=254 Hz, C-F of tfb), 133.8 [PPh$_3$ (ortho)], 131.4 [PPh$_3$ (para)], 129.6 [PPh$_3$ (ipso)], 129.2 [PPh$_3$ (meta)], 126.9 (m, bridging C$_{Ar}$ of tfb), 83.0 (s, sp^2-C of tfb) and 42.6 (s, bridgehead CH of tfb). ^{19}F NMR (CD$_2$Cl$_2$) δ: −145.6 (d, 2F, J=22.7 Hz, C-F of tfb), −152.3 (s, 4F, BF$_4$), −158.2 (d, 2F, J=22.7 Hz, C-F of tfb). ^{31}P NMR (CD$_2$Cl$_2$) δ: 28.7 (d, J_{Rh-P}=156 Hz). HRMS (FAB) calcd. for C$_{48}$H$_{36}$F$_4$P$_2$Rh (m/z): 853.1283, found: 853.1270.

[(tfb)Rh(PPh$_3$)$_2$]OTf (3e)

Catalyst **3e** was prepared by the same method as that for **3d** by using AgOTf (23 mg, 0.090 mmol) instead of AgBF$_4$. Yield: 80 mg (97%). ^{1}H NMR (CD$_2$Cl$_2$) δ: 7.43–7.31 (m, 30H), 5.86 (brs, 2H, bridgehead CH), 4.31 (brs, 4H, sp^2-CH). ^{13}C NMR (CD$_2$Cl$_2$) δ: 140.5 (dm, J=245 Hz, C-F of tfb), 138.9 (dm, J=257 Hz, C-F of tfb), 133.8 [PPh$_3$ (ortho)], 131.4 [PPh$_3$ (para)], 129.4 [PPh$_3$ (ipso)], 129.2 [PPh$_3$ (meta)], 127.0 (m, bridging C$_{Ar}$ of tfb), 121.2 (q, $^1J_{C-F}$=321.2 Hz, CF$_3$), 83.0 (s, sp^2-C of tfb), 42.6 (s, bridgehead CH of tfb). ^{19}F NMR (CD$_2$Cl$_2$) δ: 78.3 (s, 3F, OTf), −145.6 (d, 2F, J=22.7 Hz, C-F of tfb), −158.2 (d, 2F, J=22.7 Hz, C-F of tfb). ^{31}P NMR (CD$_2$Cl$_2$) δ: 28.6 (d, J_{Rh-P}=157 Hz). HRMS (FAB) calcd. for C$_{48}$H$_{36}$F$_4$P$_2$Rh (m/z): 853.1283, found: 853.1274. Anal. calcd. for C$_{49}$H$_{36}$F$_7$O$_3$P$_2$RhS: C, 58.69%; H, 3.62%, found: C, 58.43%; H, 4.03%.

Polymerization

All the polymerizations of **1a–d** were carried out under an argon atmosphere in a Schlenk tube equipped with a three-way stopcock (for polymerization conditions, see, for example, footnote a in Table 1). A THF solution of **1a–d** was added to an Rh catalyst solution of the same volume in the Schlenk tube. The polymerization solution was stirred at 30 °C for 24 h, and the formed polymer was isolated by precipitation in a large amount of methanol, including a drop of acetic acid, filtered with a PTFE membrane and dried under vacuum to constant weight.

Multistage polymerization

Three-stage polymerization of **1a** with catalyst **3a** and ^{i}PrNH$_2$ was performed by the following experiment. The first-stage polymerization was started by the addition of a **1a** (0.22 ml, 2.0 mmol) solution in THF (2.0 ml) to a solution of Rh catalyst **3a** (9.4 mg, 8.0 μmol) with ^{i}PrNH$_2$ (6.9 μl, 80 μmol) in THF (2.0 ml), which was kept at 30 °C during polymerization. After confirming the completion of the first stage by GC, a part (1.0 ml) of the polymerization solution was taken out and poured into methanol to precipitate the polymer as an orange solid. Then the second feed of **1a** (0.16 ml, 1.5 mmol) was added to the remaining polymerization solution. After complete consumption of **1a** in the second stage, an aliquot of the polymerization solution (1.0 ml) was taken out and poured into a large amount of methanol to isolate the polymer. To the remaining polymerization solution, the third feed of **1a** (0.11 ml, 1.0 mmol) was added and monitored by GC until the end of polymerization. Then the polymerization solution was poured into methanol to isolate the polymer formed at the last stage. Each of the obtained poly(**1a**)s were subjected to GPC measurement to determine their M_n and M_w/M_n.

Table 1 Polymerization of 1a with a series of cationic Rh catalysts 3a–e and 4[a]

Entry	Cat.	[^{i}PrNH$_2$]/[Rh]	Conv. (%)[b]	Polymer			
				Yield (%)[c]	M_n[d]	M_w/M_n[d]	IE (%)[e]
1	3a	0	100	95	54 000	1.40	90
2	3a	10	100	100	100 000	1.09	51
3	4	0	100	96	146 000	1.72	34
4	4	10	100	98	116 000	1.30	43
5	3b	0	100	100	202 000	1.31	25
6	3b	10	100	100	210 000	1.15	24
7	3c	0	100	100	996 000	1.58	5
8	3c	10	100	100	961 000	1.59	5
9	3d	0	100	100	600 000	2.07	9
10	3d	10	100	100	195 000	1.14	26
11	3e	0	100	100	550 000	2.22	9
12	3e	10	100	100	174 000	1.10	29

Abbreviation: Rh, rhodium.
[a]In tetrahydrofuran, 30 °C, 24 h, [1a]$_0$=0.50 M, [1a]$_0$/[Rh]=500.
[b]Determined by GC ((*tert*-butylbenzene)=50 mM as an internal standard of GC).
[c]MeOH-insoluble part.
[d]Estimated by GPC (PSt standard).
[e]Catalyst initiation efficiency.[19]

Block copolymerization

Monomer **1a** was firstly polymerized in THF for 60 min using catalyst **3a** and ^{i}PrNH$_2$. After the completion of monomer consumption was confirmed by GC, an aliquot was taken out to isolate the formed poly(**1a**) from excess MeOH, which was subjected to GPC measurement. Then, an equimolar amount of monomer **1b** or **1c** to monomer **1a** was added to the remaining polymerization solution, and the resulting solution was further stirred for 60 min (polymerization conditions: in THF, 30 °C; [monomer]$_0$=[monomer]$_{added}$=0.50 M, [monomer]$_0$/[Rh]=250, [^{i}PrNH$_2$]/[Rh]=10). The formed block copolymers were isolated in a manner similar to the homopolymer of **1a**.

RESULTS AND DISCUSSION

Our recent paper demonstrated that a zwitterionic Rh catalyst **2** is very active in polymerization of **1a** to yield poly(**1a**) with high molecular weight (M_n 180 000) (conditions: in THF, 30 °C, 24 h, [1a]$_0$=0.50 M, [1a]$_0$/[2]=500).[19] However, the obtained polymer showed rather broad MWD (M_w/M_n 1.80), suggesting the non-living character of the catalytic system. Relatively well-controlled polymerization was achieved by a cationic complex **3a**, derived from **2** (Scheme 2), which afforded poly(**1a**) with lower molecular weight (M_n 54 000) and somewhat narrower MWD (M_w/M_n 1.40) under the same polymerization conditions (Table 1, entry 1). Besides, the addition of amines such as Et$_3$N, Et$_2$NH, ^{n}BuNH$_2$, ^{i}PrNH$_2$ and pyridine to the polymerization system with **3a** was found to reduce the MWD of the formed poly(**1a**) (M_w/M_n<1.23). The narrowest MWD (M_w/M_n 1.09) with M_n of 100 000 of poly(**1a**) was accomplished by the combination of **3a** and 10 equivalents of ^{i}PrNH$_2$ (Table 1, entry 2).[21] The ^{1}H NMR confirmed that the formed poly(**1a**) with M_w/M_n of 1.09 possessed highly stereoregular *cis*-transoidal structure (*cis* content=97%) in the main chain as in the case of other Rh catalysts.[7]

The monomer consumption rate in the polymerization of **1a** with catalyst **3a** and ^{i}PrNH$_2$ was monitored (Figure 1). The polymerization proceeded in first order with respect to monomer concentration, indicating a bimolecular reaction between monomer **1a** and the propagating end. The line was found not to pass the origin, implying that the formation of active species at an early stage of the
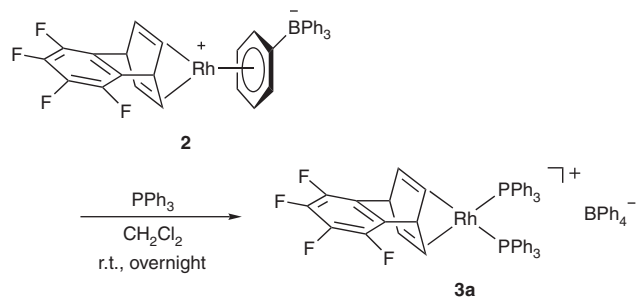
Scheme 2 Synthesis of the cationic Rh catalyst **3a** by the reaction of **2** with PPh$_3$.

polymerization requires a part of monomer **1a** and its rate is rather higher than that of propagation.

The living nature of the polymerization of **1a** by the current binary catalyst, **3a**/^{i}PrNH$_2$, was also confirmed by the multistage polymerization. In the employed three-stage polymerization of **1a** (conditions, in THF, 30 °C, [^{i}PrNH$_2$]/[Rh]=10, [1a]$_0$/[Rh]=250 and [1a]$_0$= [1a]$_{add}$=0.50 M), monomer **1a** was completely consumed at the end of each stage, confirmed by GC analyses. The second and third stages were then started by supplying **1a** to the polymerization solution. The M_n of the produced polymers increased in proportion to the consumption of monomer (M_n=55 000 (first stage), 119 000 (second) and 168 000 (third)), whereas MWDs remained in a range of small value (M_w/M_n=1.23 (first stage), 1.13 (second) and 1.17 (third)).

It is of interest to compare the catalytic activity of **3a** with that of an analogous cationic complex bearing nbd, **4** (Scheme 1). It has been reported that the highly π-acidic tfb ligand is preferable for high turnover in the propagation reaction of **1a**[17,19] and even for the synthesis of high-molecular-weight living poly(**1a**).[18] Results for the polymerization of **1a** with **3a** and **4** are displayed in Figure 1 and Table 1, entries 1–4. Both **3a** and **4** were active for the polymerization of **1a** irrespective of the presence or absence of ^{i}PrNH$_2$. Interestingly, the rate of monomer consumption with nbd-Rh catalyst **4** was faster than that with tfb-Rh catalyst **3a**. It is the opposite tendency to the results obtained using the other type of catalysts, such as [(diene)RhCl]$_2$ and zwitterionic Rh complexes.[17,19] The MWDs of the polymers obtained with **3a** were narrower than those with **4** regardless of the presence or absence of ^{i}PrNH$_2$.

A series of cationic Rh catalysts **3b–e** (Scheme 1) were investigated for the polymerization of **1a** (entries 5–12, Table 1). For observing the effect of phosphine ligand, the Rh catalysts, **3b** and **3c**, bearing more electron-donative bulky monophosphine, P(*p*-tolyl)$_3$, and bidentate phosphine, dppf, were examined. Both with and without addition of ^{i}PrNH$_2$, catalyst **3b** gave similar results to those of **3a** with respect to the MWD of the formed polymers, although the molecular weights appreciably increased (entries 5 and 6). It suggests that the number of active species derived from **3b** is smaller than that derived from **3a**. It is supported by the polymerization results using catalyst **3c** bearing a dppf ligand. The polymerization with catalyst **3c** resulted in even higher molecular weights of poly(**1a**)s regardless of the addition of ^{i}PrNH$_2$ (entries 7 and 8), probably because slow dissociation of the bidentate dppf led to the formation of small number of active propagation species. With addition of ^{i}PrNH$_2$ to catalyst **3c**, no effect of the obtained poly(**1a**) on the MWD could be observed, suggesting that ^{i}PrNH$_2$ did not accelerate the dissociation of dppf from an Rh center by ligand exchange. These tendencies are consistent with the results of the calculated initiation efficiencies described in Table 1.
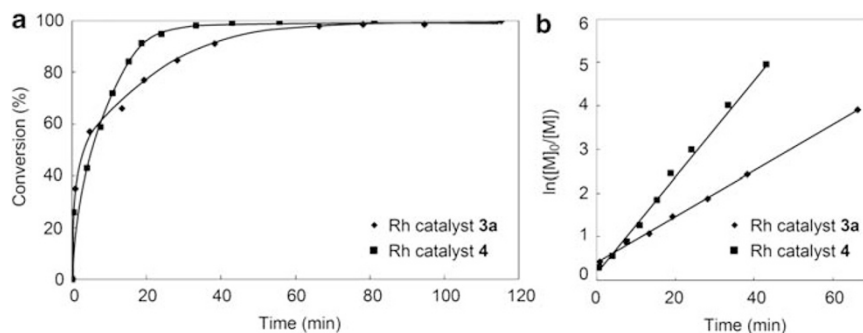
Figure 1 (a) Time-conversion curves and (b) first-order plots for the polymerization of **1a** with Rh catalyst **3a** (◆) or **4** (■) in conjunction with ^{i}PrNH$_2$ (conditions: in THF, 30 °C, [**1a**]$_0$=0.50 M, [**1a**]$_0$/[Rh]=500, [^{i}PrNH$_2$]/[Rh]=10).

The effect of the counter anion of the cationic Rh catalyst was investigated with catalysts **3d** and **3e**, having tetrafluoroborate and triflate as counter anion, respectively. Both catalysts **3d** and **3e** without amine afforded poly(**1a**)s with much higher molecular weights and broad MWDs, more than 2.0 (entries 9 and 11, respectively). In case of both **3d** and **3e**, addition of ^{i}PrNH$_2$ remarkably decreased the MWDs of the produced polymers (entries 10 and 12, respectively). However, the molecular weights of the polymers did not decrease as much as those of the **3a**-based polymer, probably because of the insufficient formation of active species from **3d** and **3e**. Thus, it can be said that the catalyst composed of **3a** and ^{i}PrNH$_2$ is the most appropriate for precise control of the polymerization among the catalysts examined.

The effect of monomer/Rh ratio ([**1a**]$_0$/[Rh]) on the polymerization was investigated by changing the catalyst concentration and keeping the monomer concentration at 0.25 M (Table 2). A monomer concentration of 0.25 M instead of 0.50 M was adopted to avoid the formation of insoluble high-molecular-weight polymers. It is noteworthy that the polymer's molecular weight increased with higher monomer/Rh ratio, whereas the monomer conversion was invariably quantitative. The MWD remained lesser than 1.2 in the range of [**1a**]$_0$/[Rh]=250–2000, supporting the living nature of polymerization. Apparent catalyst initiation efficiencies were calculated on the basis of the molecular weights (M_n), monomer/Rh ratios and yields of the formed polymers, which are displayed in Table 2. Admittedly, the IE tends to be improved with higher monomer/Rh ratio: the highest IE of 82% was achieved in the case of [**1a**]$_0$/[Rh]=4000, although MWD went broad to 1.47. It suggests that the formation of active initiator requires incorporation of **1a** and the rate of the initiation reaction is slower than that of propagation.

The effect of amine/Rh ratio was also examined by changing the [^{i}PrNH$_2$]/[Rh] ratio from 1 to 500. As seen in Table 2, the M_w/M_n remained below 1.20 in a wide range of amine/Rh (=1–250). It is noted that even 1 equivalent of ^{i}PrNH$_2$ to the Rh catalyst is effective to some extent. On the other hand, a large excess of ^{i}PrNH$_2$, such as 500 equivalents, showed a slight adverse effect. Thus, it is concluded that 10 equivalents of amine is optimal to suppress the polydispersity.

In the specific polymerizations in entries 4 and 5 of Table 2, the monomer conversion was again monitored by GC (Figure 2). It was confirmed that the polymerizations proceeded in first order with respect to monomer concentration at [**1a**]$_0$/[Rh] ratios of 1000 or 2000. Furthermore, these first-order plots exactly passed the origin unlike the cases of Figure 1. This is probably because the amount of monomer **1a** required for the formation of initiating species is negligible at such high monomer/Rh ratios. Reducing the catalyst ratio to half (from 0.25 to 0.125 mM of [Rh], Figures 2a and b,

Table 2 Effect of monomer/Rh and amine/Rh ratios on the polymerization of 1a with 3a/^{i}PrNH$_2$ catalyst[a]

					Polymer		
Entry	[**1a**]$_0$/[Rh]	[^{i}PrNH$_2$]/[Rh]	Conv. (%)[b]	Yield (%)[c]	M_n[d]	M_w/M_n[d]	IE (%)[e]
1[f]	500	10	100	100	100 000	1.09	51
2	250	10	100	100	60 000	1.11	43
3	500	10	100	98	110 000	1.10	45
4	1000	10	100	100	170 000	1.10	60
5	2000	10	100	100	310 000	1.19	66
6	4000	10	100	100	500 000	1.47	82
7	1000	1	100	100	200 000	1.15	51
8	1000	100	100	100	200 000	1.12	51
9	1000	250	100	100	200 000	1.19	51
10	1000	500	100	100	192 000	1.23	53

Abbreviations: IE, initiation efficiency; Rh, rhodium.
[a]In tetrahydrofuran, 30 °C, 24 h.
[b]Determined by GC ((*tert*-butylbenzene)=50 mM as an internal standard of GC).
[c]MeOH-insoluble part.
[d]Estimated by GPC (PSt standard).
[e]Catalyst initiation efficiency.[19]
[f][**1a**]$_0$=0.50 M.

respectively) did not result in the half rate of monomer consumption: only a slightly lower rate was observed with the half of the catalyst concentration of 0.125 mM. It indicates that the IE increases with lower catalyst concentration, consistent with the results in Table 2, entries 4 and 5.

The present catalyst consisting of **3a** and ^{i}PrNH$_2$ also showed activity in other polymerization solvents than THF. For example, when the polymerization of **1a** was carried out in toluene under the same conditions as those of entry 4, Table 2, practically the same results were obtained (in toluene: polymer yield 100%, M_n 170 000, M_w/M_n 1.10). On the other hand, CH$_2$Cl$_2$ affected the polymerization in a different way; that is, although the polymerization proceeded quantitatively, the polymer showed a higher molecular weight (M_n 300 000) and a larger MWD (M_w/M_n 1.32), suggesting a lower IE.

The following NMR experiments elucidated a part of the roles of ^{i}PrNH$_2$ in the current living polymerization. In ^{31}P NMR, complex **3a** showed a doublet at 29.6 p.p.m. in CD$_2$Cl$_2$ (Figure 3a). This doublet kept its narrow shape even in the presence of PPh$_3$ (1.1 equivalents) (Figure 3b), indicating slow ligand exchange between the coordinating and free PPh$_3$ in NMR time scale. With addition of ^{i}PrNH$_2$ (three equivalents), however, both of the signals apparently became broad (Figure 3c). With 10 equivalents of ^{i}PrNH$_2$, the two peaks almost
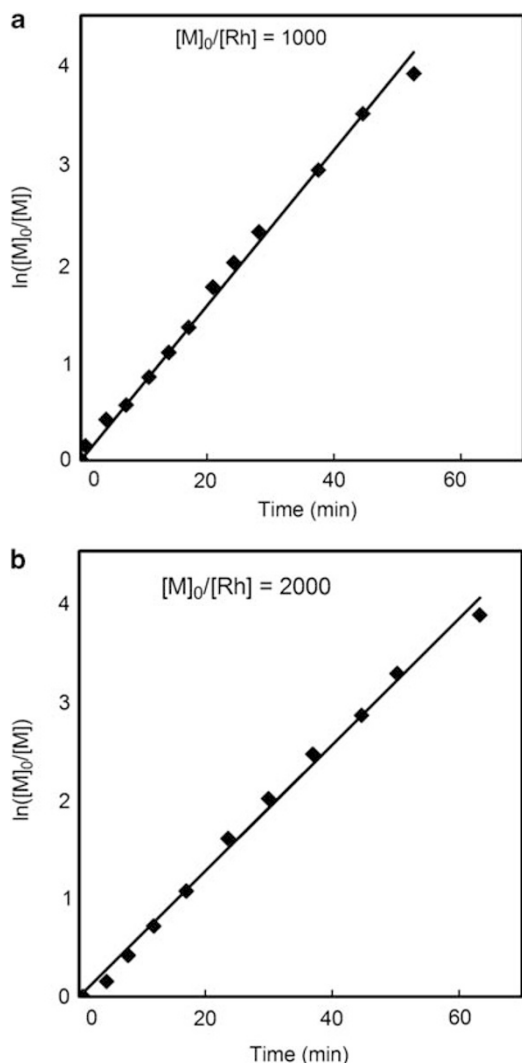
Figure 2 First-order plots for the polymerization of 1a with 3a/^{i}PrNH$_2$ catalyst (conditions: (a) [1a]$_0$=0.25 M, [1a]$_0$/[Rh]=1000, [^{i}PrNH$_2$]/[Rh]=10. (b) [1a]$_0$=0.25 M, [1a]$_0$/[Rh]=2000, [^{i}PrNH$_2$]/[Rh]=10).
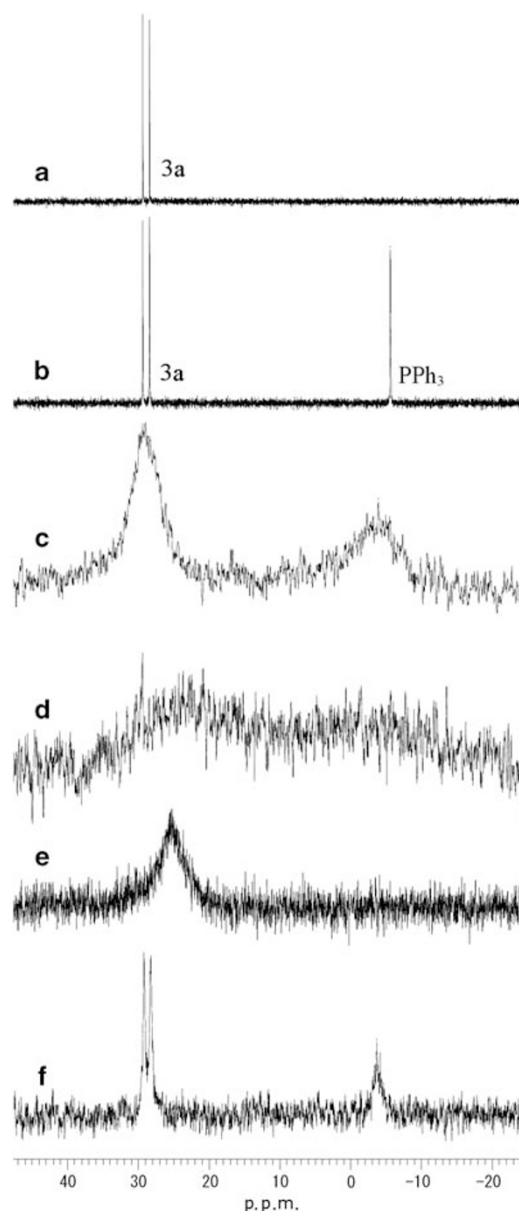

Figure 3 ^{31}P NMR spectra of (a) 3a, (b) 3a with PPh$_3$ (1.1 equiv), (c) 3a with PPh$_3$ (1.1 equiv) and ^{i}PrNH$_2$ (3 equiv), (d) 3a with PPh$_3$ (1.1 equiv) and ^{i}PrNH$_2$ (10 equiv), (e) 3a with ^{i}PrNH$_2$ (3 equiv) and (f) 3a with TMEDA (2 equiv) in CD$_2$Cl$_2$.

coalesced (Figure 3d). These results show that ^{i}PrNH$_2$ accelerates the ligands exchange between the coordinating and free PPh$_3$. A mixture of 3a and ^{i}PrNH$_2$ (three equivalents) with no addition of PPh$_3$ gave one broad peak at ca. 26 p.p.m. and did not show any signal assignable to free PPh$_3$ (Figure 3e). This is explained by the fast exchange between the major coordinating PPh$_3$ of 3a and minor dissociated PPh$_3$. Another supportive experimental result was obtained by mixing 3a with a bidentate amine ligand, N,N,N′,N′-tetramethylethylene-diamine, which shows a broad peak at ca. −4 p.p.m. assignable to free PPh$_3$ (Figure 3f).

Unfortunately, it was unable to identify the newly formed complex in the reaction of 3a with ^{i}PrNH$_2$. The ^{1}H and ^{31}P NMR of the mixture of 3a and ^{i}PrNH$_2$ in CD$_2$Cl$_2$ even at −85 °C did not give clear results to prove the formation of new Rh species, because the observed spectra at the low temperature remained almost unchanged from the one at room temperature. From the mixture of 3a and ^{i}PrNH$_2$ in CD$_2$Cl$_2$, evaporation of all volatiles perfectly reproduced 3a. A CD$_2$Cl$_2$ solution of the residue showed no other signal assignable to new species.

The results shown above indicate that ^{i}PrNH$_2$ promotes the dissociation of PPh$_3$ from 3a with its weak coordination. Thus, a

certain amine complex like [(tfb)Rh(PPh$_3$)(H$_2$N^{i}Pr)]$^+$ may presumably be formed for a short time in the mixture of 3a and ^{i}PrNH$_2$. Jimenéz et al.[24] recently demonstrated that a cationic Rh complex bearing a phosphine–amine bidentate ligand, namely, [Rh(cod){Ph$_2$P(CH$_2$)$_3$NMe$_2$}][BF$_4$], is active for polymerization of 1a. This complex forms a phenylethynyl-Rh initiating species by reaction with 1a along with the formation of an ammonium moiety on the bidentate ligand. In the present living polymerization, the same experiment could not provide sufficient evidence for the formation of a similar alkynyl–Rh complex because of the instability of the new amine complex. Assuming the formation of the analogous amine–phosphine complex, [(tfb)Rh(PPh$_3$)(H$_2$N^{i}Pr)]$^+$, a possible mechanism of the polymerization is depicted in Scheme 3.
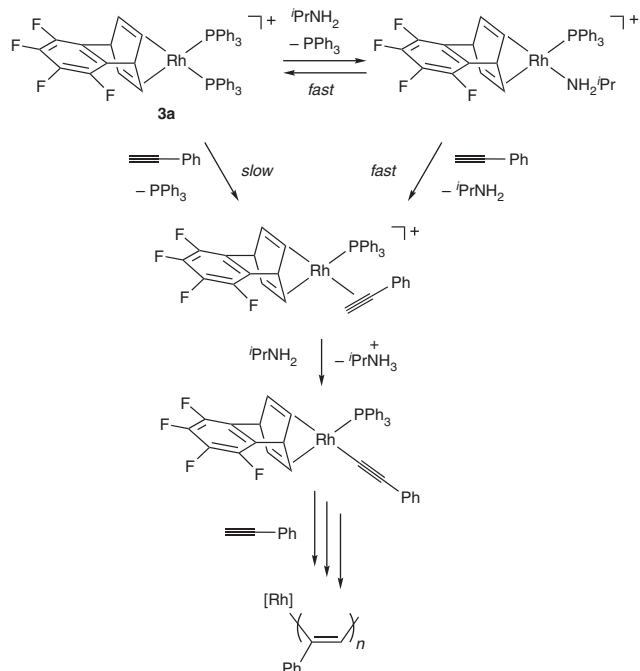
Scheme 3 Possible mechanism of the polymerization of **1a** with **3a**/^{i}PrNH$_2$. The counter anions of the cationic Rh complexes were omitted for clarity.

Table 3 Polymerization of monomers 1a–d with 3a/^{i}PrNH$_2$ catalyst[a]

| Entry	Monomer	Conv. (%)[b]	Polymer		
			Yield (%)[c]	M_n[d]	M_w/M_n[d]
1	**1a**	100	100	100 000	1.09
2	**1b**	100	100	190 000	1.40
3	**1c**	100	100	200 000	1.13
4	**1d**	40	37	20 000	1.70

Abbreviation: Rh, rhodium.
[a]In tetrahydrofuran, 30 °C, 24 h, [monomer]$_0$=0.50 M, [monomer]$_0$/[Rh]=500, [^{i}PrNH$_2$]/[Rh]=10.
[b]Determined by GC (($tert$-butylbenzene)=50 mM as an internal standard of GC).
[c]MeOH-insoluble part.
[d]Estimated by GPC (PSt standard).

To survey further application of **3a**/^{i}PrNH$_2$ system, polymerizations of monomer **1b–d** (Scheme 1) were experimented and the polymerization results are summarized in Table 3. In the polymerization of **1b** bearing a *tert*-butyl group, the catalyst **3a** with ^{i}PrNH$_2$ showed excellent activity to afford the corresponding polymer in quantitative yield with a high molecular weight of 190 000, but it exhibited relatively broad MWD (M_w/M_n 1.40) (entry 2). Monomer **1c** bearing a trimethylsilyl group also polymerized with the current living catalyst to give poly(**1c**) in excellent yield with a high molecular weight of 200 000 (entry 3). It is noteworthy that the produced poly(**1c**) showed even smaller MWD (M_w/M_n 1.13) than that of the poly(**1b**). It implies that even a slight difference of electron donativity between *tert*-butyl and trimethylsilyl can affect the control of polymerization with the current catalytic system and the trimethylsilyl-substituted **1c** is rather favored for its well-controlling the MWD. In the polymerization of **1d** having an electron-withdrawing fluoro group, the monomer could not be sufficiently consumed in the given condition to afford only 37% yield of the corresponding polymer with broad MWD (M_w/M_n 1.70)
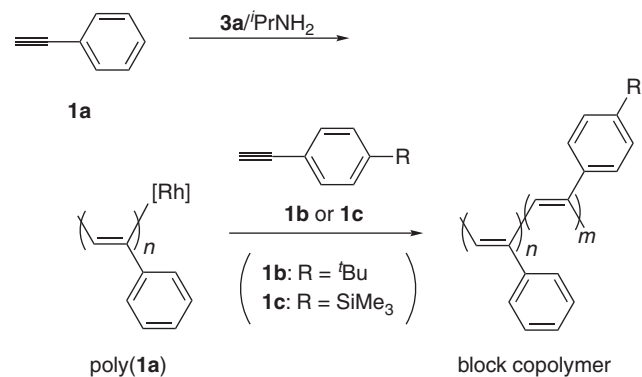
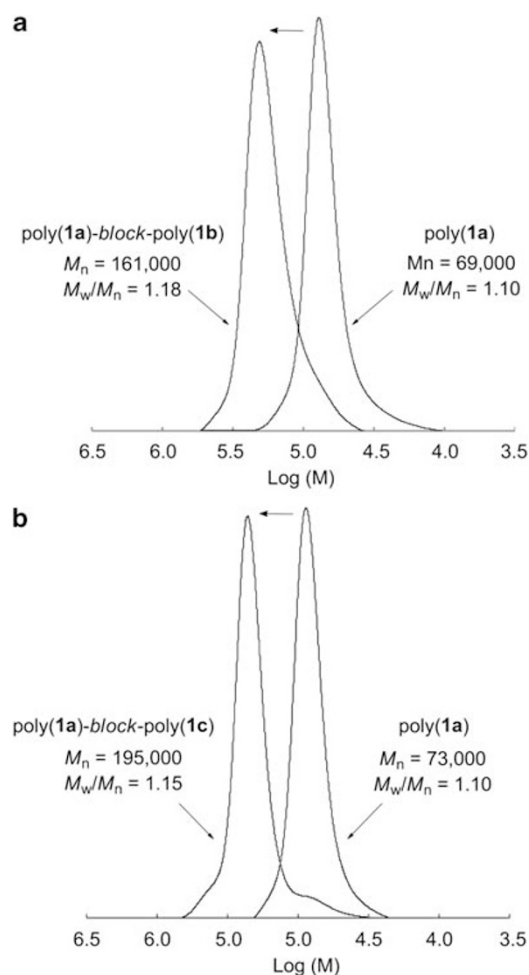**Scheme 4** Synthesis of block copolymers with **3a**/^{i}PrNH$_2$ catalyst.

Figure 4 GPC charts: (**a**) poly(**1a**) and poly(**1a**)-*block*-poly(**1b**) and (**b**) poly(**1a**) and poly(**1a**)-*block*-poly(**1c**).

(entry 4). It appears that the electron-withdrawing substituent lowers the monomer reactivity and renders living polymerization difficult.

Block copolymer synthesis
The present catalyst, **3a**/^{i}PrNH$_2$, was applied to the block copolymer synthesis by the sequential polymerization of **1a** and its derivative **1b** or **1c** (Scheme 4), which yielded the corresponding block copolymers almost quantitatively. Figure 4a shows the GPC profiles of the

first-stage homopolymer, poly(**1a**), and the second-stage block copolymer, poly(**1a**)-*block*-poly(**1b**). The first-stage polymer showed a unimodal GPC curve (M_n 69 000, M_w/M_n 1.10). The second-stage polymer also exhibited a unimodal peak in a higher-molecular-weight region (M_n 161 000, M_w/M_n 1.18), which is indicative of selective formation of the block copolymer. Poly(**1a**)-*block*-poly(**1c**) showed a GPC peak similar to that of poly(**1a**)-*block*-poly(**1b**), although a small shoulder was observed at the position of the first-stage poly(**1a**) (Figure 4b). The ratios of the monomer units in the block copolymers were calculated from the peak area ratios of aromatic and either *tert*-butyl or trimethylsilyl protons in their ^{1}H NMR spectra to be 1:1.14 (**1a**:**1b**) and 1:1.07 (**1a**:**1c**), respectively. These ratios are close to the supplied monomer ratio of 1:1.

CONCLUSIONS

A new binary catalyst consisting of [(tfb)Rh(PPh$_3$)$_2$]BPh$_4$ (**3a**) and ^{i}PrNH$_2$ proved to achieve living polymerization of phenylacetylene-type monomers. The present living polymerization is applicable to the syntheses of block copolymers composed of two types of phenylacetylene monomers. Further studies of the present Rh catalyst and living polymerization, especially the polymerization mechanism, are now in progress.

ACKNOWLEDGEMENTS

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